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Grafting of styrene onto methacrylated woods

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メタクリル化木材へのスチレンのグラフト重合

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Résumé

Reaction conditions to graft-copolymerize vinyl monomers onto the wood esterified with unsaturated carboxylic acids were studied in connection with cross-linking. Copolymerized wood samples increased in weight, only when they had been bonded with the unsaturated ester groups. Weight increase was invariably accompanied by the corresponding disappearance of the double bond. Copolymerization was enhanced by the increased accessibility of the substituents. Grafting was thus supposed to take place exclusively at the position of the accessible pendant double bonds of the esterified wood. According to infrared spectra, the degree of polymerization of the grafted side-chain was as small as four to five on the average. This disadvantage seemed not to be overcome by addition of divinylbenzene as a cross-linking agent under the conditions studied. Formation of cross-linking between wood components by the grafting could not be confirmed satisfactorily.

要　　旨

不飽和カルボン酸でエステル化した木材に，ビニルモノマーをグラフト重合し，木材構成成分の間に架橋を形成させるための条件を検討した。BPO のような開始剤を用いた今回の重合では，木材中に不飽和基が導入された時のみ，木材試料の重量が増加した。共重合の進行とともに，木材中の活性な二重結合の量は直線的に減少した。しかし，ベンゼン溶媒中の反応では，あらかじめ導入したエステル基量のおよそ 1/2 が未反応のまま残った。エステル化木材が DMSO で膨潤された場合のように，導入基のアクセシビリティーが高められている反応条件下で，重量増加が大きかった。これらの結果より，木材一不飽和酸エステルへのビニルモノマーのグラフトが生じ，その反応開始位置は主として導入されたエステル基の二重結合であることが示唆された。グラフトされた側鎖高分子の鎖長は，IR 分析より，平均 4～5 個のモノマー単位をもつ重合体に相当することが推定された。架橋剤の添加によっても，この鎖長はほとんど増大しなかった。本実験の範囲内では，グラフト重合による架橋の形成を確認できなかった。グラフトした側鎖高分子の分離とその組成分析が必要である。

1. Introduction

Berlin and Makarova[1] first showed that cellulose acetate-methacrylate esters gelled

in solution when heated with benzoyl peroxide and formed insoluble infusible copolymers when heated with acrylic ester monomers. Since that time, many investigations have been undertaken to copolymerize vinyl monomers with cellulose derivatives, into which substituent groups containing reactive double bonds such as methacryl and allyl groups were introduced.

According to the literatures available[2)-10)], the above reaction was graft-copolymerization initiated exclusively at the position of the double bond of the substituents. Cross-linking reaction between cellulose chains was suggested to take place through the grafted side-chain-polymer radicals. The graft copolymers were then assumed to have three-dimensional sturdy networks. The situations were in many respects comparable to the polymerization of unsaturated polyester resins. However, a limited degree of grafting has been encountered, even when the reaction was carried out in the homogeneous system.

It was previously reported that wood was successfully esterified with unsaturated carboxylic acids by the trifluoroacetic anhydride method.[11)] This paper deals with several reaction conditions to graft-copolymerize styrene or methyl methacrylate monomers onto the wood methacrylated by the above method, in connection with cross-linking, namely bonding the wood specimens by the grafting.

2. Experimental

2.1. *Methacrylation of wood meal*

Buna sapwood meal (*Fagus crenata* BLUME, 42 to 60-mesh) was previously extracted for 24 hr with an ethanol-benzene mixture in a Soxhlet extractor.

In a typical ester preparation[11)], the original (extracted) wood meal (10 g) was treated for 24 hr at 30°C in a pre-incubated mixture of trifluoroacetic anhydride (TFAA, 42 ml), methacrylic acid (26 ml), concentrated sulfuric acid (0.2 ml) and benzene (300 ml). The methacrylated wood (MA-wood) meal was collected on a fritted-glass crucible, washed exhaustively with de-ionized water to remove the reactants and trifluoroacetyl ester groups bonded, extracted successively with acetone and chloroform, oven-dried through air-drying, and then weighed.

Apparent acetyl content was determined for MA-wood by saponifying with 0.5 N alcoholic potassium hydroxide solution for 72 hr at room temperature. The value comprises of both the original acetyl and the methacryl (calculated as acetyl) contents.

2.2. *Polymerization procedure*

Commercial styrene was purified in the usual way, and distilled under reduced pressure with a purified nitrogen stream, immediately before polymerization[12)].

The original or MA-wood meal (0.5 g), styrene (5 ml), and a given amount of benzoyl peroxide (BPO) were put into a 50-ml glass-stoppered Erlenmeyer flask. In certain

cases, solvents and divinylbenzene (DVB) were also added, and 2,2'-azobisisobutyronitrile (AIBN) was used instead of BPO. A stream of pure nitrogen was bubbled into the mixture for several minutes to displace air roughly. The flask was then stoppered promptly and allowed to stand for a definite time in a water-thermostat controlled to 50 or 60°C. After polymerization, a large portion of homopolymer was dissolved in benzene and filtered off. Exhaustive separation of the copolymerized wood meals from homopolymer was achieved by further extraction with benzene in a Soxhlet extractor for at least 48 hr. Homopolymer was recovered by precipitation with methanol.

The amount of grafted polymer was calculated from weight increase of the wood meals. In this paper, the graft polymer possibly contains also the polymer difficult to be removed from the copolymerized wood meals by extraction alone. Degree of grafting and graft efficiency represent weight percentages of graft polymer to MA-wood meals used and total polymer formed, respectively. Conversion value is given as percentage of total polymer to monomer used.

Freshly distilled methyl methacrylate (MMA) was copolymerized similarly to the above-described grafting of styrene, except using AIBN as initiator.

2.3. *Infrared absorbancy ratio measurement*

Infrared spectra were measured with a Hitachi-EPI-G3 spectrophotometer, by the potassium bromide disk technique.

Absorbancy ratio was calculated from intensities of the two absorption bands. The bands at 705 and 810 cm^{-1}, arising from the C-H out-of-plane bending about the aromatic ring of polystyrene and the ethylene group of the methacryl group, respectively, are chosen in this paper as key bands whose intensities should vary with grafting of styrene. The control band, intensity of which has to remain unchanged during copolymerization, is one at 1740 cm^{-1} owing to the ester C=0 stretching vibration of the methacryl group.

3. Results and discussion

3.1. *Copolymerization conditions*

The utility of the double bond of the methacryl group introduced into wood is considered to be indispensable for cross-linking and bonding wood specimens by chain polymerization catalyzed by initiators such as BPO and AIBN. Then, experiments were at first carried out to determine the extent of participation of the substituent group in graft copolymerization.

Table 1 shows that in most cases, the methacrylated woods acquire a relatively large degree of grafting. The same reaction conditions other than different degrees of substitution (DS) of MA-woods elicit necessarily a large polymer-weight-gain for the esterified

Table 1 Grafting of styrene onto the original and methacrylated BUNA wood meal

Polymerization condition			Degree of grafting (%)	Graft efficiency (%)	Conversion (%)
Wood meal	Initiator (mg)	Benzene (ml)			
MA-wood[a)]	None	10	1.1	30.8	0.4
	BPO, 47	0	17.3	8.6	23.0
		5	11.2	7.3	16.8
		10	8.4	6.7	13.9
	BPO, 94	0	31.2[b)]	3.7	92.1
		0	20.1	6.6	34.2
		5	12.5	5.8	23.4
		10	9.4	5.5	19.9
	AIBN, 64	10	8.3	3.4	26.5
Original	None	10	0.2	5.4	0.4
	BPO, 47	0	0.0	0.0	24.8
		5	0.7	0.5	16.6
		10	2.1	1.6	14.4
	BPO, 94	0	1.6	0.5	34.9
		5	0.8	0.4	22.9
		10	2.4	1.4	19.9
	AIBN, 64	10	3.7	1.3	28.5

wood meal 0.5 g, styrene 5 ml, initiator, and benzene as a solvent, at 50°C for 24 hr

a) methacrylated wood of 14.2% wt. inc. (15.4% app. Ac content)

b) at 60°C

wood meals than for the original one. The data suggest that the presence of the methacryl group favours the augmentation in the degree of grafting. On the other hand, a slight degree of grafting obtained for the original wood may be attributed to a small amount of homopolymer left after extraction with benzene rather than a truly-formed graft polymer.

Polymerization of styrene, conversoin curves in Fig. 1, proceeds linearly until a conversion value of about 100 % is

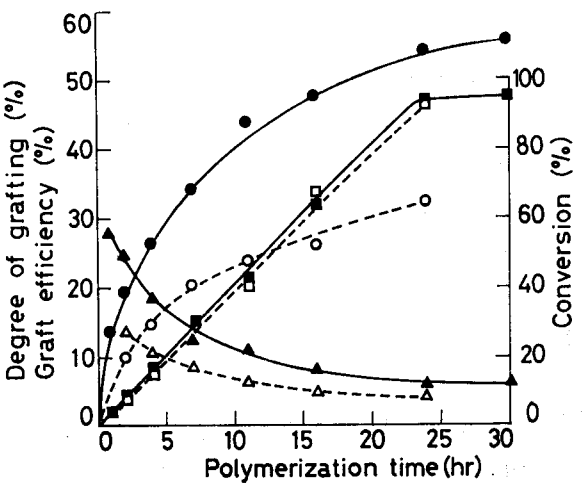

Fig. 1. Grafting of styrene onto methacrylated BUNA wood meal
○ degree of grafting △ graft efficiency
□ conversion
MA-woods of 23.4% (—) and 14.2% (- - -) wt. inc. 0.5 g, styrene 5 ml, and BPO 94 mg, at 60°C

reached. The rate of polymerization is little changed by using MA-wood meals of different DS values, when the other reaction conditions are definite. However, the rate of grafting (copolymerization) and the maximal degree of grafting are appreciably different in two wood meals having different ester contents, as seen from both curves for the degree of grafting. The latter value appears especially to be correlated with the DS of MA-wood. Such dependence on the DS is clearly visualized in Fig. 2, where the degree of grafting increases linearly with increasing apparent acetyl content in the region of more than 8 % (dark circles). According to the fact that the value 8 % agrees roughly with the acetyl content of the original Buna wood[13], it follows that the maximal degree of grafting is directly proportional to the amount of the methacryl group introduced in advance. This was also confirmed by the linear relationship between the degree of grafting and the weight increase by esterification.

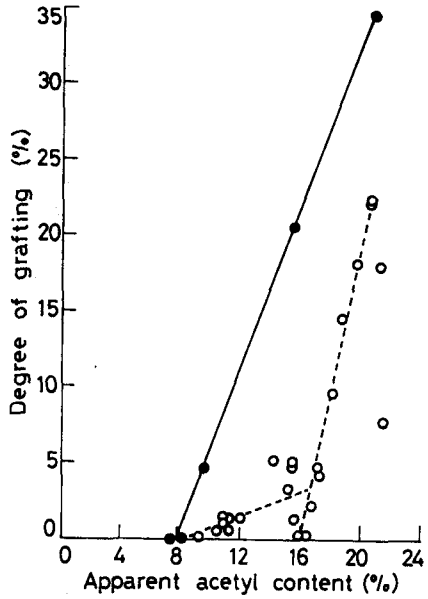

Fig. 2. Relation between degree of grafting and apparent acetyl content
0.5 g of MA-BUNA wood meals prepared just before use (●) and allowed to stand for a long time after preparation (○), styrene 5 ml, and BPO 94 mg, at 60°C for 7 hr

The above results indicate that addition (or graft)-copolymerization of styrene to MA-wood meal is initiated at the position of pendant ester groups, perhaps through their active double bonds under the conditions investigated. By comparison of the reactivity of cellulose acetates to MMA with that of cellulose acrylate-acetates, Matsuzaki and his co-workers[3] have concluded that the grafting of MMA takes place exclusively at the position of the double bond of acryl groups in the cellulose mixed esters. A role of an unsaturated ester group as an initiation site of grafting has also been demonstrated by Miyata et al.[9]. According to them, the initial rate of grafting increases with the DS of cellulose methacrylates.

Fig. 2 further shows stability of the double bond of the methacryl group in MA-wood. The degree of grafting is fairly larger for the methacrylated woods grafted immediately after preparation (dark circles) than the corresponding esters allowed to stand for more than one year in contact with air prior to reaction (empty circles). It is evident that a long-term exposure to air at room temperature rather slowly inactivates the sub-

Table 2 Effects of solvents on grafting of styrene to methacrylated BUNA wood meal

Solvents	Degree of grafting (%)	Graft efficiency (%)	Conversion (%)	Absorbancy ratio[a]	
				$A_{C=C}/A_{C=O}$	$A_{PSt}/A_{C=O}$
	—	—	—	1.53[b]	0
None	54.2	5.8	93.3	0.71	1.05
Dioxane	53.5	9.7	53.8	0.55	1.09
Acetone	56.9	12.1	47.1	0.55	1.17
Ethanol	61.8	10.2	56.9	0.57	1.26
Pyridine	60.6	15.9	39.6	0.39	1.27
DMAc[c]	51.1	13.3	39.0	0.59	1.07
DMF[d]	48.9	13.3	37.4	0.63	0.89
DMSO[e]	28.2	19.2	14.3	0.93	0.63

MA-wood meal of 23.4% wt. inc. (20.7% app. Ac content) 0.5 g, styrene 5 ml, BPO 94 mg, and solvent 5 ml, at 60°C for 24 hr

a) $A_{C=O}$, $A_{C=C}$ and A_{PSt} are absorbancy of bands at 1740, 810 and 705 cm^{-1}, respectively

b) for the not-grafted MA-wood meal

c) dimethylacetamide d) dimethylformamide e) dimethyl sulfoxide

Table 3 Grafting of methyl methacrylate onto the original and methacrylated BUNA wood meal

Polymerization condition			Degree of grafting (%)	Graft efficiency (%)	Conversion (%)
Wood meal	Initiator (mg)	Benzene (ml)			
MA-wood[a]	AIBN, 32	0	35.5	4.6	83.9
	AIBN, 64	0	29.1	3.5	91.3
		5	15.5	1.8	96.2
		10	10.9	1.5	79.2
Original	AIBN, 32	0	5.4	0.6	88.2
	AIBN, 64	0	2.6	0.3	91.0
		5	0.0	0.0	95.6
		10	0.0	0.0	79.1

wood meal 0.5 g, MMA 5 ml, AIBN and benzene as a solvent, at 50°C for 24 hr

a) methacrylated wood of 14.2% wt. inc.

stituent groups against copolymerization with styrene. A relatively high stability of the double bond of substituents in derivatives of sugars and cellulose has been reported by Zief and Yanovsky[14] and others[8].

Other factors affecting the grafting of styrene and MMA onto MA-wood meal are shown in Tables 1, 2 and 3. In the tables, calculation indicates that 0.5 g of MA-wood meals of 14.2 and 23.4 % weight increases, used mainly in the experiments, contains 0.72 and 1.11 mmoles of methacryl groups, respectively. The values of 43.4, 46.8, 0.38 and 0.38 mmoles are calculated for 5 ml of styrene, 5 ml of MMA, 94 mg of BPO, and 64 mg of AIBN, respectively.

One example in Table 1 shows that the rate of polymerization of styrene is

undoubtedly accelerated by increased temperature. A final degree of grafting seems almost unchanged, regardless of the reaction temperature.

Both BPO and AIBN are efficient initiators for grafting of styrene to MA-wood meals (Table 1). Nevertheless, BPO was mainly used in the present study, because a larger grafting was brought about by BPO rather than by AIBN. Increased addition of BPO accelerates the rate of polymerization of styrene to some extent, but does not increase the grafting so much. This may be due to a restricted supply of styrene monomer in the neighborhood of the methacryl group as a grafting site inside a MA-wood solid in the present heterogeneous system, a presumed retardation of termination, or equimolecular amounts of BPO and the methacryl group as calculated above.

Effects of solvents other than benzene on grafting are summerized in tables. Conversion values reveal that all the solvents used, including benzene in Table 1, reduce the polymerization of styrene to different extents. Addition of the solvents other than benzene gives the degree of grafting comparable to that of the control (no solvent) run, but gives far less conversions than the control (more than 90%) under the same reaction conditions. Graft copolymerization to mixed esters of cellulose has successfully been carried out in a homogeneous system, in which both starting materials and products were dissolved[3]. A similar homogeneous solution, where reactants are easily accessible to each other, can not be prepared in the case of MA-wood meal. However, the reactants must be brought as close as possible by the use of an appropriate swelling solvent. In Table 2, solvents except benzene are known to be relatively good swelling agents for wood[15]. They evidently give the increased degrees of grafting. Thus, the enhanced graftings should depend upon the augmentation in the pendant double bond actually accesible for copolymerization, derived from the increased swelling of MA-wood meal by the solvents. The poor result with benzene must be owing to its weak swelling power for wood. That is, a large part of the unsaturated ester group can not be reactive in the wood, as discussed in more detail later. A fairly large degree of grafting can eventually be obtained, when the polymerization is forced to completion in the presence of swelling solvents. Besides the swelling effect mentioned above, Trommsdorff effect[16] and induced decomposition of initiators[17] are considered as other reasons for the increased grafting. Solvents may also affect the degree of polymerization of side-chain polymers formed and their distribution[9].

That the methacrylated wood meal was copolymerized with styrene more readily than the acrylated one was (Fig. 3) is compatible with the observations of Corbett and McKay[8]. Grafting of MMA is somewhat inferior to that of styrene, but the rate of polymerization of MMA is remarkably higher. The other results are similar to those of styrene (Tables 1 and 3). Especially, addition of excess initiator and benzene as a solvent are not effective but sometimes disadvantageous for grafting.

3.2. *IR spectroscopy of the grafted wood meal*

The foregoing discussions of polymerization conditions prove that only the factors which permit a higher accessibility of the pendant double bond in MA-woods are effective for enhancing the grafting. The others are merely a cofactor, even though the rate of polymerization is often affected largely. The extent of the substituent group copolymerized is evaluated by the infrared spectroscopy of the grafted woods.

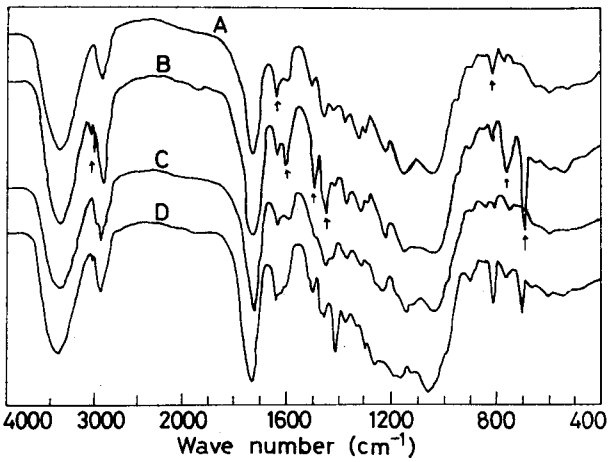

Fig. 3. Infrared spectra of BUNA woods esterified with methacrylic and acrylic acids and their graft-copolymers with styrene and MMA
methacrylated wood of 23.4% wt. inc. (A), its copolymer with styrene (degree of grafting 34.6%, B), its copolymer with MMA (35.5%, C), and acrylated wood of 21.2% wt. inc. grafted up to 13.2% with styrene (D)

Infrared spectra of MA-wood meal grafted with styrene exhibit new prominent bands which appear at 705, 760, 1450, 1500, 1600 and around 3000 cm^{-1}, evidently arising from the aromatic ring and the methylene group of polystyrene (Fig. 3). In addition, two characteristic bands at 810 and 1640 cm^{-1} owing to the C=C unsaturated group of the methacryl group are still observed in wood-polystyrene composite. Their intensities are, however, diminished to some extent by copolymerization. The fact implies the disappearance of a part of the pendant double bond in MA-wood during the course of polymerization, but does not reveal whether all of the double bonds consumed is actually concerned with grafting.

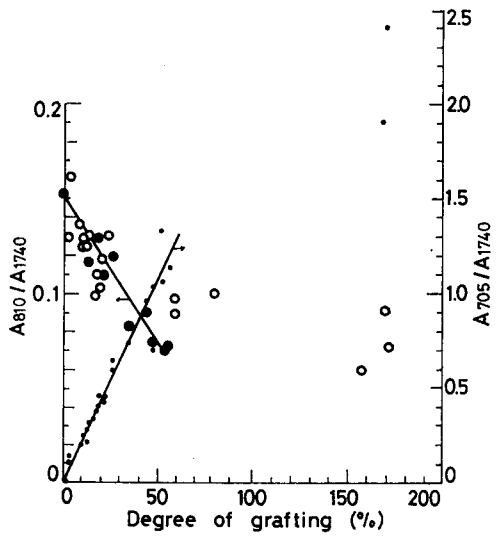

Fig. 4. Dependence of absorbancy ratios for the double bond of the methacryl ester group (○, ●) and the grafted polystyrene (・) upon degree of grafting
MA-BUNA wood 0.5 g, styrene 5 ml, and BPO 94 mg, with DVB of 0.1–0.4 ml (○) and without DVB (●), at 60°C for 0.5–5 hr

Absorbancy ratios are plotted against the degree of grafting in Fig. 4. The band at 1740 cm^{-1} is due to the

ester groups (acetyl and methacryl groups), those at 810 and 705 cm^{-1} referring to the methacryl group irresponsible for grafting and the grafted polystyrene, respectively. The ratio is reasonable in the present case, because two different expressions of the grafted polystyrene, namely the degree of grafting based on weight increase and the absorbancy ratio of 705 to 1740 cm^{-1} (A_{705}/A_{1740}), bear a good linear relationship.

The amount of the double bond remaining (A_{810}/A_{1740}) decreases almost linearly with increasing degree of grafting, although some scatter is present in the figure, probably because of a relatively small intensity of the band at 810 cm^{-1}. The two absorbancy ratio curves show that the increase in polystyrene is invariably accompanied by the corresponding decrease in the double bond. Considering the foregoing fact that wood having no unsaturated groups can not gain weight increase, it is concluded that the weight increase was caused by a real grafting, and not by a mere incorporation of homopolymer; that is, the grafting took place at the position of the double bond, and its extent was closely related to the amount of the bond consumed.

Fig. 4 shows also that the reaction of the double bond is restricted. Only one half of the initial unsaturated ester groups is reactive in the absence of the swelling solvent. It may be due to the fact that formation of cross-linking prevents monomers from penetrating and a remaining ester group from polymerizing, as hardening of unsaturated polyesters[18]. It is calculated that about one methacryl group is present per one cellobiose unit in MA-wood of 25 % weight increase. In a sense, this amount is presumed to be too much for complete copolymerization. Or else, it may be attributed to the location of the ester group in wood cell wall where they can not easily come into contact with monomers. The latter is more plausible, and seems to be consistent with the above-cited stability of the double bond, the larger penetrating ability of acids used for esterification than monomers and that the magnitude of the restriction was changed by the use of swelling solvents. Fifth and sixth columns in Table 2 indicate that such good swelling solvents for wood as pyridine enhance the degree of grafting, because of the raised accessibility of the double bond.

A linear relationship between the double-bond consumption and the increase in the grafted polystyrene suggests that the reactivity of the pendant methacryl group to styrene monomer remained constant in the course of polymerization. Under this situation, resulting copolymers would have an analogous monomer composition. Calculated molar ratio of the methacryl group to styrene is about 1:5 for MA-wood of 23.4% weight increase, when copolymerized up to the degree of grafting of 54% with styrene. Therefore, the grafted side-chain polystyrene must be too short to bond wood specimens. Hamann and co-workers[18] have reported that hardening of unsaturated polyesters with styrene results in cured products composed of networks of a similar short chain-length of cross-

Table 4 Grafting of styrene onto methacrylated BUNA wood meal, in the presence of divinylbenzene (DVB)

Polymerization time (hr)	DVB added (ml)	Degree of grafting (%)	Graft efficiency (%)	Conversion (%)
0.5	0.1	3.4	22.5	1.6
	0.2	3.1	17.5	2.0
1	0	12.9	28.2	5.1
	0.2	11.6	28.9	4.4
2	0	19.6	25.0	9.1
	0.1	19.4	23.5	9.3
	0.2	18.4	22.5	8.8
	0.3	48.9	37.0	14.6
	0.4	157.5	45.4	36.9
3	0.1	20.7	21.3	11.2
	0.2	48.3	33.5	16.0
4	0	26.7	18.8	16.5
	0.2	171.0	74.6	25.1
5	0.2	168.7	59.2	31.5

MA-wood meal of 23.4% wt. inc. 0.5 g, styrene 5 ml, BPO 94 mg, and DVB, at 60°C

linked polystyrene.

The formation of cross-linking can not be deduced from the above data alone. Copolymerization with DVB was then carried out to increase the possibility of cross-linking (Tables 4 and Fig. 4). In the region of lower degree of grafting below 50%, DVB-added runs do not differ greatly from those not containing DVB in the consumption of the double bond; the chain-length of the grafted polystyrene is still short. On the other hand, sufficient grafting in the presence of DVB gives a longer side-chain polymer by calculations. However, the calculated value is doubtful, because wood-polystyrene composites should include a relatively large amount of homopolymer which can not sufficiently be dissolved out by benzene extraction, on account of its three-dimensional network structure. Formation of cross-linking and effectiveness of DVB on it are still uncertain, and a further study is necessary on copolymers recovered from the composites. Analytical data will be reported in the near future.

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